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MOLECULAR MOTION AND ENERGY MIGRATION IN POLYMERS(U)
ROYAL INSTITUTION OF GREAT BRITAIN LONDON (ENGLAND)
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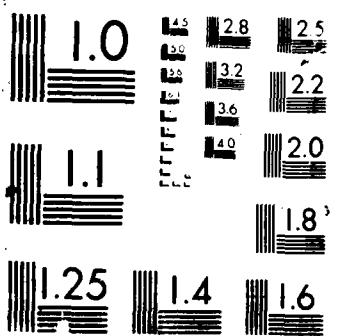
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MOLECULAR MOTION AND ENERGY MIGRATION IN POLYMERS

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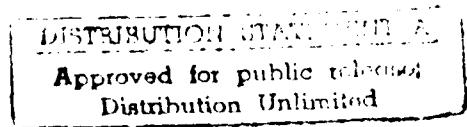
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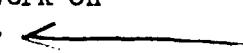
Contract Number DAJA 37-82-C-0265

Fourth Periodic Report

January 1984 - June 1984

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Three aspects of the work in hand are reported briefly below. We have continued our investigation of energy migration in poly(styrene) by making some steady-state and time-resolved fluorescence anisotropy measurements. Secondly, we have continued to use such methods to investigate segmental motion in vinyl naphthalene tagged poly(methyl methacrylate and methyl acrylate polymers. Finally, the work on conducting polymers, poly(diacetylenes) has been extended. 

Energy Migration in poly(styrene)

Our earlier extensive work on excimer formation in poly(styrene)¹ and copolymers², together with the use of a poly(styrene) doped with a phenyl oxazole (PPO) fluorescent tag³, led to the conclusion that electronic energy migration along a chain of phenyl groups was a facile process. This conclusion is incompatible with the results of MacCallum^{4,5}, who suggested that the steady-state fluorescence anisotropy of poly(styrene) in both solid state and dilute solution was of the order of 0.2, whereas after extensive energy migration this figure would be zero. We have therefore reinvestigated the anisotropy of this polymer in dilute solution, the medium in which our earlier work was performed.

MacCallum first reported the anisotropy as 0.7⁴, which is impossible unless the system is oriented⁶. He later quoted a figure of 0.2⁵, without referring to his own earlier measurement of 0.7. Gupta et al, by contrast, state that fluorescence from poly(styrene) in the solid state is completely depolarized⁷. Our own results are tabulated below⁸ (Table 1). We find quite clearly that the fluorescence of poly(styrene) excimer, and that of the PPO trap in the tagged polymer, is completely depolarized when styrene is excited selectively, but that upon excitation of the trap directly polarization of PPO trap emission is observed compatible with time-resolved measurements reported earlier⁹. The most likely explanation for this depolarization of emission in poly(styrene) is the occurrence of energy migration.

We have almost completed a further study of excimer formation in copolymers of styrene-acrylonitrile, and in collaboration with Dr. Alan Fawcett, Queens University Belfast, have begun an investigation of the fluorescence of copolymers of styrene and sulphur dioxide. These studies will be reported fully in the next periodic report.

Time-resolved fluorescence anisotropy in poly(methyl methacrylate) and poly(methyl acrylate)

An extensive study of the temperature dependence of the time-resolved anisotropy of fluorescence arising from copolymers of methylmethacrylate and methyl acrylate with vinyl naphthalene and acenaphthylene has been completed. A typical set of results on one polymer is shown in Table 2, and plotted as an Arrhenius plot in Figure 1. The slope of the lines obtained for all four polymers are given in Table 3.

A-1

Table 1

Degree of fluorescence polarization in polystyrene solutions.

Method	Sample	$\lambda_{\text{exc.}}$ /nm	λ_{em} /nm	P
Laser	PS	257.25	335	0.005 ± 0.050
Steady-state	PS	265	335	0.005 ± 0.020
Steady-state	POS (0.058%)	265	335	-0.006 ± 0.020
	POS (0.11%)	265	335	0.026 ± 0.020
	POS (0.504%)	265	335	0.027 ± 0.020
Steady-state	POS (0.058%)	265	380	0.040 ± 0.020
	POS (0.11%)	265	380	0.047 ± 0.020
	POS (0.504%)	265	380	0.048 ± 0.020
Steady-state	POS (0.058%)	320	380	0.135 ± 0.020
	POS (0.11%)	320	380	0.134 ± 0.020
	POS (0.504%)	320	380	0.144 ± 0.020

Table 2

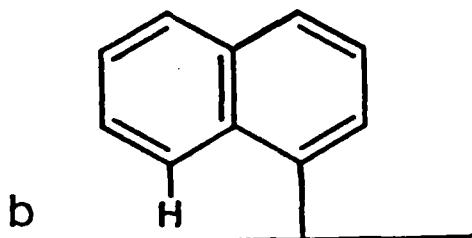
Summary for Polymethylacrylate labelled with
1-vinylnaphthylene fluors in dichloromethane

T/K	$\frac{1}{T}$ (K ⁻¹)	$\tau_{\text{rot}}/\text{ns}$	$\frac{1}{\tau_{\text{rot}}}$ (sec)	$\ln(\frac{1}{\tau_{\text{rot}}})$	$\tau_{\text{FL}} \text{ ns}^{-1}$	τ_0
295 ± 2	(3.38 ± 3.05) $\times 10^{-3}$	0.4 ± 0.2	(3 ± 1) $\times 10^9$	21.7 ± 0.6	15.1 ± 0.1	0.11 ± 0.01
274 ± 2	(3.64 ± 3.03) $\times 10^{-3}$	0.8 ± 0.1	(1.29 ± 0.2) $\times 10^9$	20.9 ± 0.1	14.9 ± 0.1	0.12 ± 0.02
260 ± 2	(3.8 ± 3.03) $\times 10^{-3}$	1.0 ± 0.2	(1.19 ± 0.1) $\times 10^9$	20.8 ± 0.1	14.8 ± 0.1	0.11 ± 0.01
245 ± 2	(4.08 ± 3.04) $\times 10^{-3}$	1.3 ± 0.2	(0.89 ± 0.2) $\times 10^9$	20.5 ± 0.2	14.9 ± 0.1	0.13 ± 0.01
230 ± 2	(4.35 ± 3.04) $\times 10^{-3}$	1.7 ± 0.3	(0.69 ± 0.1) $\times 10^9$	20.2 ± 0.1	14.9 ± 0.1	0.15 ± 0.01

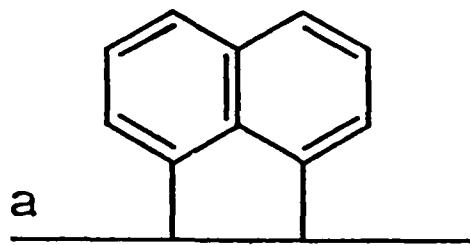
Table 3
Arrhenius parameters

Polymer	Slope of $\ln \frac{1}{\tau_{\text{rot}}}$ vs $\frac{1}{T}$	Correlation coeff.
Polymethyl methacrylate		
Acenaphthylene	$-(1.5 \pm 0.2) \times 10^3$ $\Delta E = 12 \pm 2 \text{ kJ mol}^{-1}$	-0.994
1-vinyl naphthalene	$-(1.4 \pm 0.1) \times 10^3$ $\Delta E = 12 \pm 1 \text{ kJ mol}^{-1}$	-0.992
Polymethyl acrylate		
Acenaphthylene	$-(1.1 \pm 0.1) \times 10^3$ $\Delta E = 9 \pm 1 \text{ kJ mol}^{-1}$	-0.990
1-vinyl naphthalene	$-(1.02 \pm 0.03) \times 10^3$ $\Delta E = 8.5 \pm 0.2 \text{ kJ mol}^{-1}$	-0.988

These slopes yield activation energies for the depolarizing motion shown in the table. It is seen that there is little discernible difference between the results obtained with the two probes, which is perhaps surprising given the fact that in the case of the poly(vinyl naphthalene), the naphthalene moiety is singly bonded to the polymer backbone, (I) whereas in the case of the acenaphthalene, the two bonds in the α , α' positions (II) might have led to the expectation of more restricted motion in this case. The difference in activation energy between methyl methacrylate and methyl acrylate polymers is a clear reflection of the different flexibilities of these polymers. A complete report on this work is in preparation.



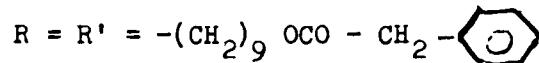
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Luminescence of Conducting Polymers

Fluorescence studies in polydiacetylenes (PDAs, $(R'C-C\equiv C-CR)_n$) were initiated to gain an understanding of exciton dynamics and decay in quasi one-dimensional systems. A series of experiments are one of the class of soluble polymers obtained from the bis-ester of 10, 12-docosadiyne-1, 22-diol^{10,11} 9PA which has the chemical formula



have been conducted^{12,13}. 9PA exhibits very similar spectral profiles to the widely-studied urethane sidegroups polymers: mBCMU ($R=R' = -(CH_2)_mOCO - NH - COO - C_4H_9$) where $m = 3$ or 4 ^{14,15}. Results indicate that the transformation of PDA chains from a random coil to an ordered form is a more general phenomenon that does not necessarily require the formation of hydrogen bonds between the sidegroups as the driving force¹³. We have recently initiated some studies on 4BCMU glasses (77K). The spectral profiles displayed by this polymer are very similar to our earlier reported results of 9PA glasses³ - (Refer to Figures 2 and 3). A more detailed investigation of 4BCMU-glass is in progress.

AB: MAYS1.001

$\lambda_e = 460.0 \text{ nm}$

Figure 2
43CMU

Polymer Concentration:

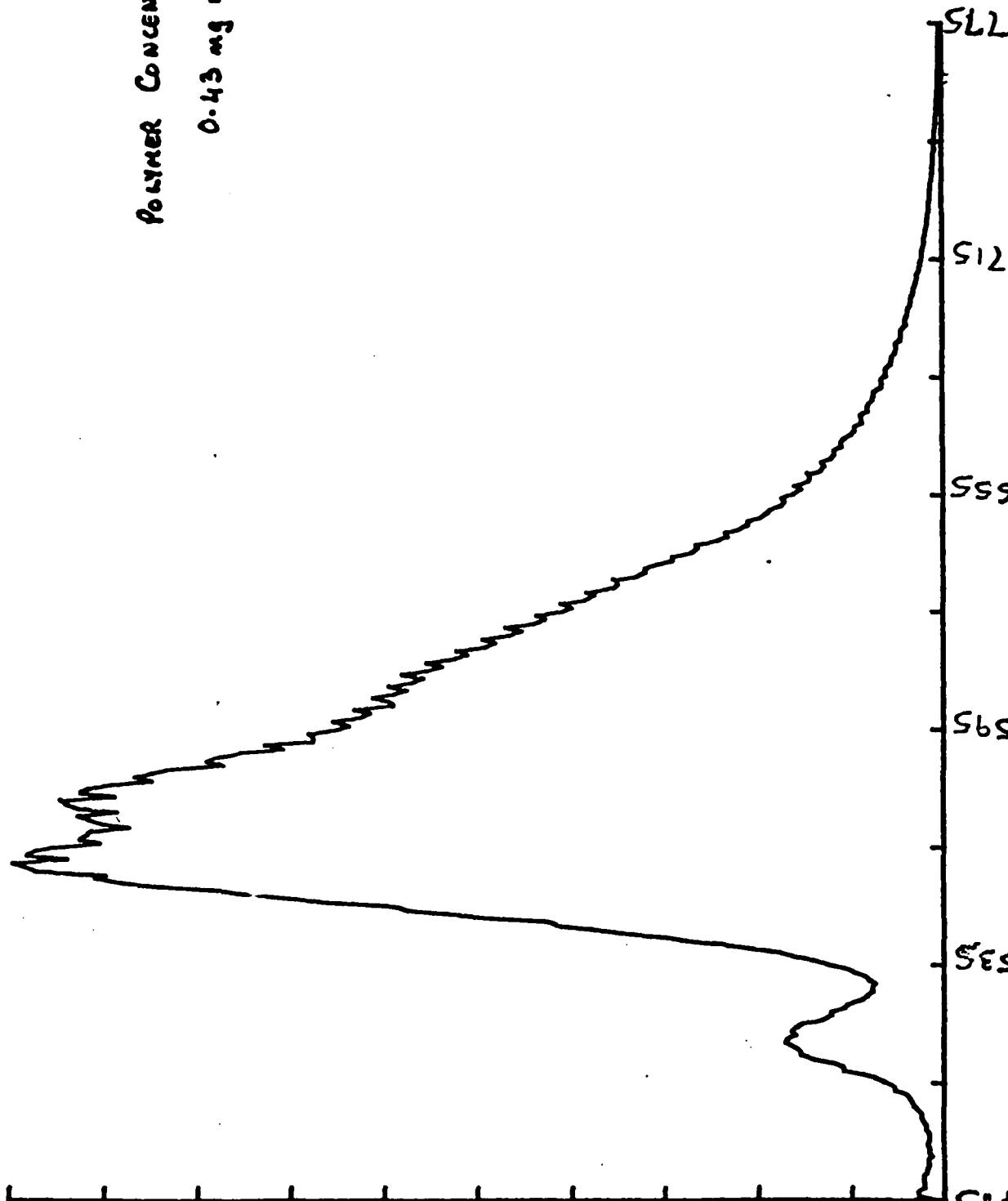
0.43 mg ml^{-1}

EMISSION (ABS. UNITS)

512
555
595
635
675

572

WAVELENGTH (nm)



AB:MYSS3.001

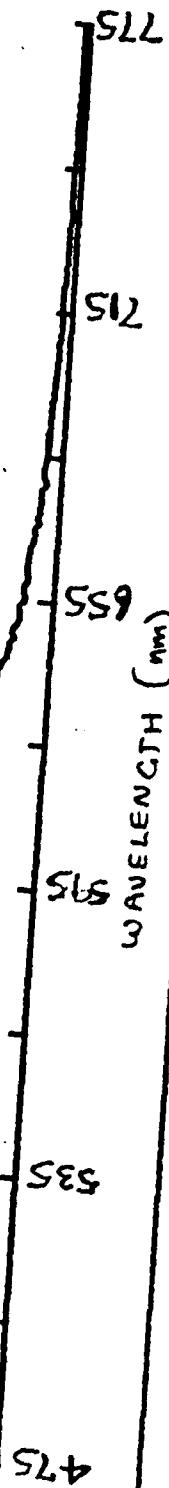
$\lambda_2 = 460.0 \text{ nm}$

Figure 3

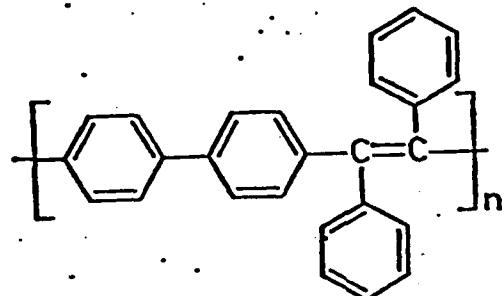
48CMU

Polymer Concentration:
 $4.3 \times 10^{-3} \text{ mg ml}^{-1}$

EMISSION (ARB. UNITS)



In collaboration with Dr. J. Feast, University of Durham, and Dr. Richard Friend, University of Cambridge, we have contributed briefly to the investigation of fluorescence in another conducting polymer poly (4,4'-diphenylene di phenyl vinylene) (III) PDPV.



3

PDPV is a soluble conjugated polymer that shows a degree of conjugation similar to that in polyparaphenylene. The optical properties of thin films exposed to AsF_5 show the appearance of features below the $\pi-\pi^*$ gap at 3 eV that can be interpreted in a model of dopant-induced polaron and bipolaron defects. When excited above the $\pi-\pi^*$ gap, PDPV shows a strong luminescence peaked at 2.4 eV. The Stokes' shift of 1 eV can be accounted for by radiative decay from photogenerated polaron-exciton defect.

However, this explanation of the observed effects may not be unique, and further work is being carried out to elucidate the cause of the very large Stokes shift in fluorescence. The quantum yield of fluorescence has been shown to be of the order of 0.01, with a decay time of around 100ps. This work will continue.

2. The remainder of the contract will be carried out on the work specified originally, and above.

Papers published or presented during Grant period.

1. 'Time-resolved fluorescence anisotropy measurements on poly(vinyl aromatic polymers)'
R.C. Drake, R.L. Christensen and D. Phillips.
Polymer Photochemistry (1984), 5, 141-151.
2. 'Excimer formation and energy transfer in vinyl (aromatic) polymers'
D. Phillips and G. Rumbles.
Polymer Photochemistry (1984), 5, 153-170.
3. 'Spectroscopic studies of poly(diacetylene) solutions and glasses'.
S.D.D.V. Rughoooph, D. Phillips, D. Bloor, and D.J. Ando.
Chem. Phys. Letters, (1984), 106, 247.
4. 'Time-resolved fluorescence spectroscopy on poly(N- G- carbazolyl) carbonyl-L-lysine (PKL) a conformationally 'pure' polymer'.
A.J. Roberts, L.L. Chapoy, D. Phillips and D. Biddle.
Chem. Phys. Letters, (1984), 103, 271.

3. The principal investigations lectured on the subject of this research at the Spring meeting of the Japan Chemical Society, Tokyo; at Nogoya and Kyoto Technical Universities, and the University of Tokyo in April 1984. He also lectured at Queens University, Belfast, and the New University of Ulster, Coleraine; The Institute for Organic Chemistry, Bulgarian Academy of Sciences, Sofia, and Ecole Polytechnique Superieur, Lausanne, Switzerland in June 1984 on this and related topics.

There have been no changes in personnel or direction of the work since the last report.

Annex

5(a) The balance of unused funds remaining on the contract at the end of June 1984 is 19490.00 \$US.

(b) Funds were expended upon partial support for Dr J-L Gardette, computational facilities, materials, refrigerants, and optical components.

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